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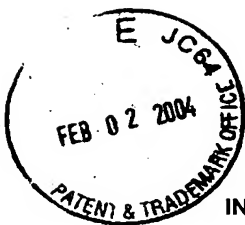
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Patent  
Attorney Docket No. 003301-052

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
MIKHAIL KEJZELMAN et al.  
Application No.: 10/689,688  
Filing Date: October 22, 2003  
Title: IRON-BASED POWDER

Group Art Unit: 1742  
Examiner: Unassigned  
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Sir:

The benefit of the filing date of the following priority foreign application(s) in the following foreign country is hereby requested, and the right of priority provided in 35 U.S.C. § 119 is hereby claimed.

Country: Sweden

Patent Application No(s): 0203133-4

Filed: October 22, 2002

In support of this claim, enclosed is a certified copy(ies) of said foreign application(s). Said prior foreign application(s) is referred to in the oath or declaration. Acknowledgment of receipt of the certified copy(ies) is requested.

Respectfully submitted,

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# PRV

PATENT- OCH REGISTRERINGSVERKET  
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## IRON-BASED POWDER

### FIELD OF THE INVENTION

The present invention relates to new metal powder compositions useful within the powder metallurgical industry. The invention also concerns a method for the preparation of high density metal components by using these compositions.

There are several advantages by using powder metallurgical methods for producing structural parts compared with conventional machining processes of full dense steel. Thus, the energy consumption is much lower and the material utilisation is much higher. Another important factor in favour of the powder metallurgical route is that components with net shape or near net shape can be produced directly after the sintering process without costly shaping processes, such as turning, milling, boring or grinding. However, normally a full dense steel material has superior mechanical properties compared with PM components. This is mainly due to the occurrence of porosity in the PM components. Therefore, the strive has been to increase the density of PM components in order to reach values as close as possible to the density value of a full dense steel.

Among the methods used in order to reach higher density of PM components the powder forging process has the advantage that full dense components may be obtained. The process is however costly and is utilised mainly for mass production of heavier components, such as connection rods. Full dense materials can also be obtained by elevating the pressure, such as in hot isostatic pressing, HIP, but also this method is costly.

By using warm compaction, a process where the compaction is performed at an elevated temperature, typically at 120 to 250 °C, the density can be increased with about 0,2 g/cm<sup>3</sup>, which results in a considerable improvement of the mechanical properties. A disadvantage is however that the warm compaction method involves additional investment and processing. Other processes, such as double pressing, double sintering, sintering at elevated temperatures etc, may further increase the density. Also these methods will add further production costs hence reducing the overall cost effectiveness.

In order to expand the market for powder metallurgical components and utilise the advantages with the powder metallurgical technique there is thus a need for a simple, less expensive method of achieving high density compacts with improved mechanical properties.

### Summary of the invention

It has now unexpectedly been found that high density components can be obtained by using high compaction pressures in combination with a new type of powders. Specifically these powders are distinguished by coarse particles, the surfaces of which have been subject to modification. The present invention also includes a method of preparing green and optionally sintered compacts from these powders. This method comprises the steps of providing an iron-based powder having coarse and surface modified particles; optionally mixing said powder with graphite and other additives; uniaxially compacting the powder in a die at high pressure and ejecting the green body, which may subsequently be sintered.

### Detailed description of the invention

The term "high density" is intended to mean compacts having a density of about at least  $7.3 \text{ g/cm}^3$ . "High density" is not an absolute value. A typical achievable density according to the state of the art for single pressed, single sintered components is about  $7.1 \text{ g/cm}^3$ . By using warm compaction an increase of about  $0.2 \text{ g/cm}^3$  may be reached.

In this context the term "high density" is intended to mean compacts having a density of about  $7.35\text{--}7.65 \text{ g/cm}^3$  and above, depending of type and amount of additives used, and type of iron-based powder used. Components having lower densities can of course also be produced but are believed to be of less interest.

The iron-based powder according to the present invention includes pure iron powder, such as water or gas atomised iron powder, sponge iron powders, *reduced* iron powder, partially diffusion-alloyed steel powder, and completely alloyed steel powder. The partially diffusion-alloyed steel powder is preferably a steel powder alloyed partially with one or more of Cu, Ni, Mo. The completely alloyed steel powder is preferably a steel powder alloyed with Mn, Cu, Ni, Cr, Mo, V, Co, W, Nb, Ti, Al, P, S and B. Also stainless steel powders are of interest.

As regards the particle shape it is preferred that the particles have an irregular form as is obtained by water atomisation. Also sponge iron powders have irregularly shaped particles and are of particular interest.

A critical feature of the invention is that the powder used have coarse particles i.e. the powder is essentially without fine particles. The term "essentially without fine particles" is intended to mean that less than about 5 % of the powder particles have a size below  $45 \mu\text{m}$  as measured by the method described in SS-EN 24 497. So far the most interesting results have been achieved with powders essentially consisting of particles above about  $106 \mu\text{m}$  and particularly above about  $212 \mu\text{m}$ . The term "essentially consisting" is intended to mean that at least 10 %, preferably at least 40 %, most preferably at least 60 % of the particles have a particle size above  $106$  and  $212 \mu\text{m}$ , respectively. So far the best results have been obtained with powders having a particle size above about  $212 \mu\text{m}$  and only less than 5 % below  $212 \mu\text{m}$ . The maximum particle size may be about 2 mm.

The particle size distribution for iron-based powders used at PM manufacturing is normally distributed with a gaussian distribution with a median particle diameter in the region of 30 to  $100 \mu\text{m}$ . A certain content of finer particles is recommended as these particles acts as so called "sintering aids". Metals Handbook, ninth ed., vol 7, p 317, teaches that "a smaller grain size (or smaller particle size) aids sintering densification and final properties."

Iron based powders essentially free from fine particles may be obtained by removing the finer fractions of the powder or by manufacturing a powder having the desired particle size distribution. As the powders used according the present invention differ from those conventionally used one would expect that problems would be encountered when the components are sintered.

The influence of particle size distribution and the influence of particle shape on the compaction properties and properties of the compacted body have been subjected to intense studies. Thus the US patent 5,594,186 reveals a method of producing PM components with a density higher than 95 % of theoretical density by utilising substantially linear, acicular metal particles having a triangular cross section. Such particles are suitably produced by a machining or milling process. Powders having coarse particles are also used for the manufacture of soft

magnetic components. Thus the US patent 6 309 748 discloses a ferromagnetic powder, the particles of which have a diameter size between 40 and 600  $\mu\text{m}$ . In contrast to iron based powder particles according to the present invention, these powder particles are provided with a coating. In the US patent 4,190,441 a powder composition for production of sintered soft magnetic components is disclosed. In this patent the iron powder includes particles with less than 5 % exceeding 417  $\mu\text{m}$ , and less than about 20 % of the powder particles have a size less than 147  $\mu\text{m}$ . This powder is mixed with specific amounts of ferrophosphorus in order to obtain the soft magnetic components.

The particles should preferably be treated with a surface modifying agent, which may be selected from the group consisting of organo alkoxysilanes, organo silazanes, fluorine-containing silicon silane coupling agents, titanate coupling agents, Zr and Al coupling agents, fatty acids, particularly saturated and unsaturated fatty acids having 10 to 24 C atoms in the alkyl chain, e.g. stearic acid, oleic acid, fatty acid esters, such as glyceryl monostearate, fatty acid amides, particularly saturated fatty acid mono- and bisamides, such as stearic monoamide, EBS, unsaturated fatty acid mono- and bisamides, such as oleic monoamide, EBO, mixed fatty acid amides, fatty acid derivative mixtures, and metal soaps. Especially preferred are alkylalkoxy silanes wherein the alkyl group has between 10- 24 carbon atoms or fatty acids with 11-25 carbon atoms. Most preferred are hexadecyltrimethoxy silane and stearic acid. Multilayer and composite layers of the above mentioned surface modifying agents may also be used.

Different methods may be used for the surface modifying of the iron based powder. According to one method the surface modifying agent can thus be dissolved or dispersed in a suitable solvent, e.g. an organic solvent, such as acetone and ethanol. The obtained solution or dispersion is subsequently added to the iron based powder during mixing and optionally heating. The solvent is finally evaporated optionally in vacuum. Alternatively, the surface modification may be performed by melting a solid surface modifying agent, mixing the heat melted surface modifying agent with a heated iron-based powder mixture followed by cooling during mixing. Heating may of course also be applied to a premixed mixture of iron-based powder and surface modifying agent. The modifying agent may be applied by spraying.

According to a preferred embodiment of the invention and contrary to common practise in powder metallurgy, where conventional PM lubricants are used in the iron powder mix, or where a lubricant is used in combination with binder and/or surface treatments, such as described in EP 1160032, the surface modified iron based powder must not be mixed with a lubricant before it is transferred to the die. Nor is it necessary to use external lubrication (die wall lubrication) where the walls of the die are provided with a lubricant before the compaction is performed. The invention however does not exclude the possibility of, when it is of interest, to utilise conventional internal lubrication, external lubrication or a combination of both.

For some applications it may be necessary to add minor amounts of graphite to the powder mixture to be compacted. Thus graphite in amounts between 0.1 - 1.0, preferably 0.2 - 1.0 and most preferably 0.3-0.8 % by weight of the total mixture to be compacted should be added before the compaction.

Other additives which may be added to the iron-based powder before compaction such as alloying elements comprising Mn, Cu, Ni, Cr, Mo, V, Co, W, Nb, Ti, Al, P, S and B machinability enhancing compounds, hard phase material and flow agents.

The term "at high compaction pressure" is intended to mean at pressures of about at least 800 MPa. More interesting results are obtained with higher pressures such as pressures above 900, preferably above 1000, more preferably above 1100 MPa.

Conventional compaction at high pressures, i.e. pressures above about 800 MPa with conventionally used powders including fine particles, are generally considered unsuitable due to the high forces required in order to eject the compacts from the die, the accompanying high wear of the die and the scratchy components obtained. By using the new powders according to the present invention it has unexpectedly been found that the ejection force is reduced at high pressures, about 1000 MPa, and that components having acceptable or even perfect surfaces may be obtained.

The compaction may be performed with standard equipment, which means that the new method may be performed without expensive investments. The compaction is performed uniaxially and preferably in a single step at ambient or elevated temperature. Alternatively the compaction may be performed with the aid of a percussion machine (Model HYP 35-4 from Hydropulsor) as described in patent publication WO 02/38315.

The sintering may be performed at the temperatures normally used within the PM field, e.g. at low temperature such as 1100-1140 or higher temperatures such as 1250°C and in conventionally used atmospheres or vacuum.

Other treatments of the green or sintered component may as well be applied, such as green machining, case hardening, surface densification, steam treatment.

In brief the advantages obtained by using the method according to the present invention are that high density green compacts can be cost effectively produced. The new method also permits production of higher components which are difficult to produce by using the conventional technique. Additionally standard compaction equipment can be used for producing high density compacts having acceptable or even perfect surface finish.

Examples of products, which suitably can be manufactured by the new method, high performance structural parts such as connecting rods, cam lobes and gears. By using stainless steel powders flanges are of special interest.

The invention is further illustrated by the following examples.

#### Example 1

Iron-based powder composition prepared from AstaloyMo, which is a prealloyed iron based powder alloyed with 1.5 % by weight of molybdenum available from Höganäs AB, Sweden, and where particles less than 212 µm had been eliminated was treated with 0.1 and 0.15 %, respectively, of a hexadecyl trimethoxysilane as a surface modifying agent. The surface modifying process was performed as follows: hexadecyl trimethoxysilane was diluted in ethanol to a 20 % solution, by weight, and the solution was stirred during 60 minutes. An amount of this solution corresponding to 0.1 and 0.15 % by weight, respectively, was added during mixing to the iron based powder mixtures, which had previously been heated to 75 °C in the mixer. An intensive mixing was carried out in the same mixer during 3 minutes followed by mixing at a lower speed during 30 minutes and during vacuum in order to evaporate the solvent. The obtained mixture was sieved with a 500 µm sieve.

Rings with an inner diameter of 35 mm and an outer diameter of 14 mm and a height of 10 mm were uniaxially compacted in a single step at different compaction pressures. As can be seen from figure 1-1 green densities of 7.67 g/cm<sup>3</sup> were obtained at a pressure of 1100 MPa for both compositions. The total energy needed for ejection is somewhat lower for the compacts prepared from the composition with 0.15 % of surface modifying agent than for ejection of the compacts prepared from the powder which had been treated with 0.1 % by weight of surface modifying agent, see figure 1-2.

#### Example 2

The same powder and the same procedure as in Example 1 was used except that the powder was treated with 0.2 % by weight of hexadecyl trimethoxysilane. Two compositions were prepared, one with 0.2 % by weight of graphite and the other with 0.6 % by weight of graphite. The green density and the green strength were measured.

As can be seen from figure 2-2 a green density above 7.65 g/cm<sup>3</sup> was obtained for a green component containing 0.2 % graphite compacted at 1200 MPa. For a green component containing 0.6 % graphite a green density of 7.58 g/cm<sup>3</sup> was obtained.

Figure 2-1 shows that the green strength increases with increasing compaction pressure and that the green strength is high enough to allow handling of the green components.

#### Example 3.

This example shows the effect of a different surface modifying agent, namely stearic acid compared with hexadecyl trimethoxysilane used in an amount of 0.2%.

The same iron-based powder as in example 2 was used with 0.2 % by weight of graphite. The surface modifying procedure for hexadecyl trimethoxysilane was the same as in example 2. For stearic acid the following surface modifying process was used: The stearic acid was dissolved in acetone for the preparation of a 5 % by weight solution. An amount of this solution corresponding to 0.2 % of stearic acid was added to the iron based powder mixture, which had previously been heated to 45°C, during mixing. An intensive mixing was carried out in the same mixer during 3 minutes followed by mixing at a lower speed during 30 minutes and during vacuum in order to evaporate the solvent. The obtained mixture was sieved with a 500 µm sieve.

Rings with an inner diameter of 35 mm, an outer diameter of 14 mm and a height of 12.7 mm were produced and the green density and ejection force were measured.

Figure 3-1 shows that about the same green density is obtained with powders having particles with a silane modified surface as with powders, the particles of which have been modified with stearic acid.

Figure 3-2 shows that the ejection force needed for ejecting the compacts increases from a compaction pressure of 800 MPa to a compaction pressure of 1000 MPa. Further increase in compaction pressure to 1200 MPa unexpectedly reduces the force needed for the ejection of the compact from the die. This figure also shows that the powders having particles with a silane modified surface require less ejection force than powders the particles of which have been modified with stearic acid.



### Example 4

**This example shows the effect of the eliminating different fractions of the surface modified iron based powder. four different iron based powder compositions were tested. Three of the iron based powder compositions contained surface modified Astaloy Mo, surface modified with the aid of 0.2 % hexadecyl trimethoxysilane and the surface modifying procedure in example 3 was used. The first composition contained Astaloy Mo coarser than 45 $\mu$ m, the second composition contained Astaloy Mo coarser than 106  $\mu$ m and the third composition contained Astaloy Mo coarser than 212  $\mu$ m. The fourth composition contained Astaloy Mo having particles coarser than 212 $\mu$ m. The particles of this composition was surface-modified with 0.1 % by weight of hexadecyl trimethoxysilane. Further, all compositions contained 0.2 % of graphite. All compositions were uniaxially compacted in a single step in a die forming rings with an outer diameter of 35 mm, inner diameter of 14 mm and a height of 10 mm.**

Figure 4-1 shows that the green densities increased and the ejection forces decreased with increasing particles sizes.

Figure 4-2 shows that the ejection forces decrease when the amount of surface modifying agent is increased from 0.1 to 0.2 % by weight.

## CLAIMS

1. Iron-based powder, the particles of which modified with a surface-modifying agent and which powder is essentially free from fine particles.
2. Iron-based powder according to claim 1 wherein that less than about 5 % of the powder particles have a size below 45  $\mu\text{m}$ .
3. Iron-based powder according to claim 2 wherein at least 10 %, preferably at least 40 % and most preferably at least 60 % of the iron-based powder consists of particles having a particle size above about 106  $\mu\text{m}$ .
4. Iron-based powder according to claim 3 wherein at least 10 %, preferably at least 40 % and most preferably at least 60 % of the iron-based powder consists of particles having a particle size above about 212  $\mu\text{m}$ .
5. Iron-based powder according to any of claim 2-4 admixed with a minor amount of graphite.
6. Iron-based powder according to any of claims 1-5 wherein the surface-modifying agent is selected from the group consisting of surface modifying agent, which may be selected from the group consisting of organo alkoxysilanes, organo silazanes, fluorine-containing silicon silane coupling agents, titanate coupling agents, Zr and Al coupling agents, fatty acids, fatty acid esters, fatty acid amides, mixed fatty acid amides, fatty acid derivative mixtures and metal soaps.
7. Iron-based powder according to claim 6 wherein the surface-modifying agent is selected from alkylalkoxy silanes or alkylsilazanes, wherein the alkyl group has between 10- 24 carbon atoms, and fatty acids with 11-25 carbon atoms.
8. Iron-based powder according to any of claims 1-7 wherein the surface modifying agent is added in an amount of 0.05- 0.5 %, preferably between 0.1- 0.4 % and most preferably between 0.15- 0.3 % by weight.
9. Iron-based powder according to any of claim 1-8 wherein the iron-based powder has irregularly shaped particles.
10. Iron-based powder according to any of claim 1-9 wherein the iron-based powder is produced by water atomisation.
11. Iron-based powder according any one of claim 1-9, wherein the iron-based powder is a sponge iron powder.
12. Iron-based powder according to any of claim 1-11 wherein the iron-based powder is selected from the group consisting of pure iron powder, a pre-alloyed iron powder and diffusion alloyed iron powder.

13. Process for the preparation of high density green compacts comprising the following steps:
- providing an iron-based powder, the particles of which are modified with a surface-modifying agent and which powder is essentially free from fine particles;
  - optionally mixing said powder with graphite and other additives;
  - uniaxially compacting the powder in a die at a compaction pressure of at least about 800 MPa; and
  - ejecting the green body.
14. Process according to claim 13, wherein the additives are selected from the group consisting of alloying elements comprising Mn, Cu, Ni, Cr, Mo, V, Co, and W, Nb, Ti, Al, P, S, and B, machinability enhancing compounds, hard phase material and flow agents.
15. Process according to any one of the claims 13-14, wherein the compaction is performed at a pressure of at least 800 MPa, more preferably at least 900 and most preferably above 1000 MPa.
16. Process according to any one of the claims 13-15, wherein the compaction is performed at ambient temperature.
17. Process according to any one of the claims 13-15, wherein the compaction is performed at elevated temperature.
18. Process according to any one of the claims 13-17 for preparing sintered products, said process further including a single sintering step at a temperature above 1100°C.
19. High performance structural parts such as connecting rods, gears, cam lobes and flanges, having a high density and prepared from coarse iron-based powder as defined in any one of the claims 1-12.

**ABSTRACT**

The present invention concerns an iron-based powder, the particles of which modified with a surface-modifying agent and which powder is essentially free from fine particles. The invention also concerns a process for the preparation of high density green compacts comprising the steps of mixing said powder with graphite and optionally other additives; uniaxially compacting the powder in a die at a compaction pressure of at least about 800 MPa and ejecting the green body.

## Example 1

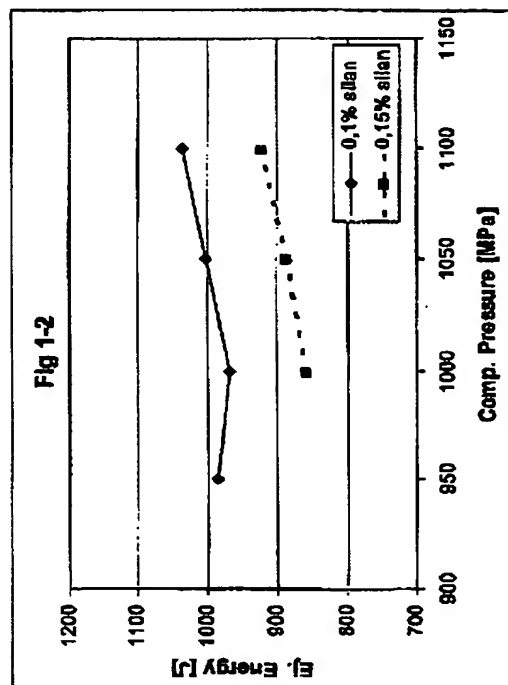
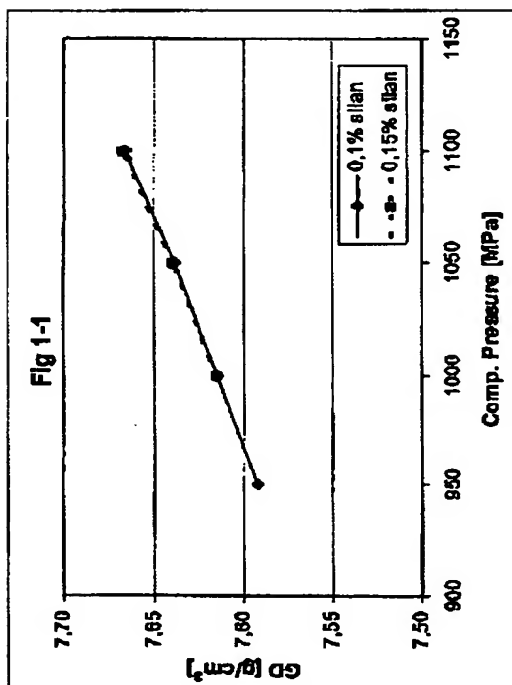
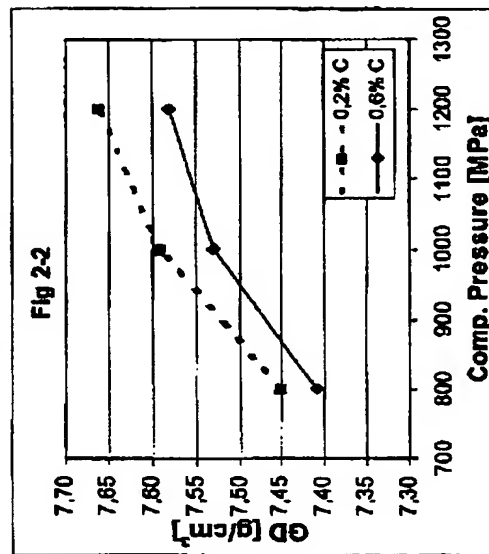
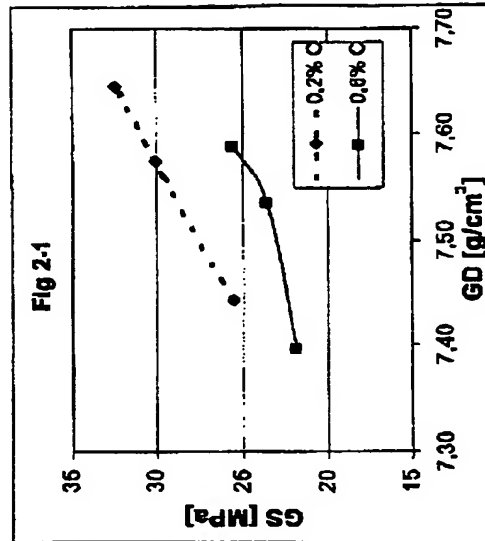


Fig. 2-1

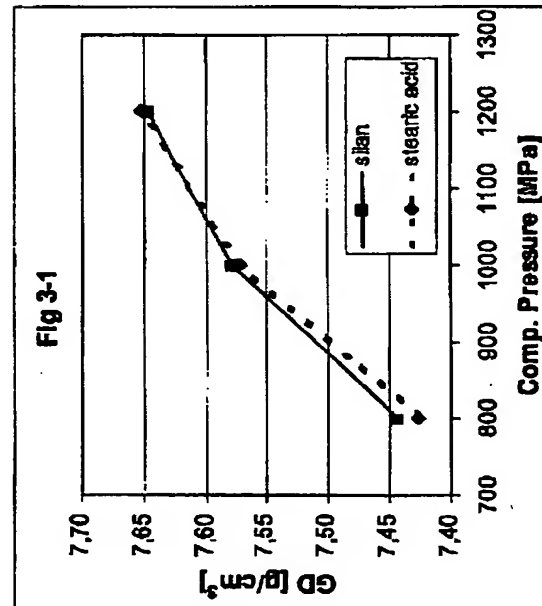
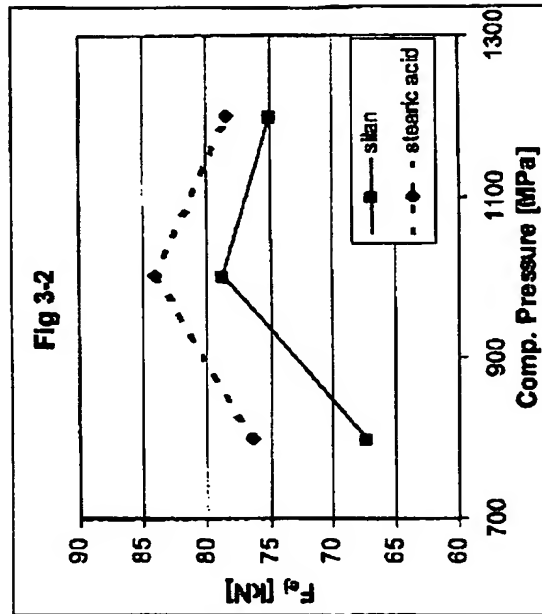
Fig. 2-2

Fig. 2-3



## Example 2

### Example 3



### Example 4

